

The Role of Seabed Dynamics in Controlling the Distribution and Preservation of Polycyclic Aromatic Hydrocarbons (PAHs) in Estuarine Sediments

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LONG-TERM GOALS

The overall goal of this study is to examine the role that energy regime and associated seabed dynamics (e.g., frequency and depths of resuspension) play in controlling the distribution of polycyclic aromatic hydrocarbons (PAHs) in estuarine sediments.

OBJECTIVES

Our objectives are to examine sediment PAH distributions in environments representing contrasting depositional regimes within the York River, VA, a sub-estuary of the Chesapeake Bay. The study utilizes a suite of geochemical tools to quantify sediment processes influencing the distribution of dissolved and solid-phase PAHs. These tools will enable us to quantify particle residence times in surface sediments, determine rates of sediment accumulation and disturbance, and investigate the effects of sediment organic matter composition and diagenesis.

APPROACH

Most of the PAHs produced by incomplete combustion of organic matter or spillage of petroleum by-products ultimately enter aquatic environments where they eventually accumulate in sediments. PAHs are thought to be relatively stable in moderately-impacted sediments, particularly under anoxic conditions. However, sediments are often disturbed both by natural processes (storms, tidal and wave resuspension, bioturbation) and human activities (dredging, ship wakes, etc.). These processes can stimulate organic matter degradation by reoxygenating sediments, promoting desorption of particle-associated organic matter, removing metabolites, and introducing labile organic matter that promotes degradation of more refractory components by co-metabolism (Aller 1998). Our project seeks to

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understand the effects of seabed mixing on the long-term capacity of sediments to sequester one class of contaminants, the PAHs.

Sediment cores were collected from sites removed from point sources and representing contrasting seabed mixing regimes to examine the role of physical disturbance on PAH fate. Since sources of PAHs to sediments of the York River are similar to those for lower Chesapeake Bay (Dickhut et al., 2000), we proposed that differences between the sites would be due to differences in the frequency and intensity of sediment mixing processes. To test our hypothesis, PIs Canuel and Dickhut and graduate student K. Arzayus characterized the sediment geochemistry at each site and measured downcore concentrations of PAHs and organic compounds covering a range in reactivity. Kuehl and graduate student T. Kniskern were responsible for quantifying the sediment mixing and accumulation rates within high and low energy regions of the York River estuary.

WORK COMPLETED

Over the past three years, a series of coordinated activities have supported our efforts to quantify the sediment accumulation and disturbance patterns within the York River as well as examine how seabed processes influence sediment PAH distributions. For the sediment processes component of the project, cores were characterized using x-radiography, water content, elemental analysis and radioisotope distributions (Be-7, Pb-210, Cs-137). On the basis of these results, two sites were selected for investigating the effects of seabed mobility on PAH abundance and composition. Paired box cores and kasten cores were collected from each site. Redox conditions within the sediments were determined within each core. The cores were sectioned and select horizons from all of the cores were extracted for PAH and organic geochemical analyses.

Sediment Dynamics

An across-channel transect near Ferry Point (upstream of Gloucester Point) is described by a spring-neap time-series (63 cores) of ^{210}Pb , ^{137}Cs , ^7Be , x-radiographs, sidescan sonar, and current meter data for 1999. Four subenvironments were identified based on the average maximum ^{137}Cs penetration depth and the character of excess ^{210}Pb profiles: physically dominated southern shoal, flank, secondary channel, and main channel (Fig. 1). Various combinations of long- and short- term events (e.g. spring-neap tidal cycle, spring freshet, storms) influence subenvironment sediment structure and physical mixing depths. Shoal sediments were eroded/deposited on the spring-neap cycle during the early spring months, whereas the other three subenvironments were not noticeably influenced by tides. Shortly after the peak currents of the annual spring freshet, sediments were temporarily deposited on the shoal and flank. Major events, such as Hurricane Floyd, did not affect this section of the river except as result of subsequent longitudinal sediment transport along the estuary main channel.

Kasten cores (13) and sidescan sonar images were also collected from the lower York River in January of 1999 and show the increasing influence of biological mixing towards the mouth of the estuary. Bioturbation structures and radioisotope data indicate that the seabed of the lower York is not subject to physical mixing as frequently as the upper York River and/or the increase in salinity allows for a more complex benthic community. Mixed layer depths in the channel are highest in the funnel zone of the York River (Ferry Point and Gloucester Point) and lowest at West Point (Dellapenna, 1999) and the mouth, supporting the Schaffner et al. (2001) proposal that there is an energy maxima between West Point and the mouth of the river. This pattern is contrary to the characteristic interrelationship between energy regime and substrate generally expected (Nichols et al., 1991; Dalrymple et al., 1992).

Overall, our study indicates that the seabed at the upper York transect is frequently physically disturbed on a variety of time scales, whereas the lower York is dominated by biological mixing, with less frequent physical disturbance.

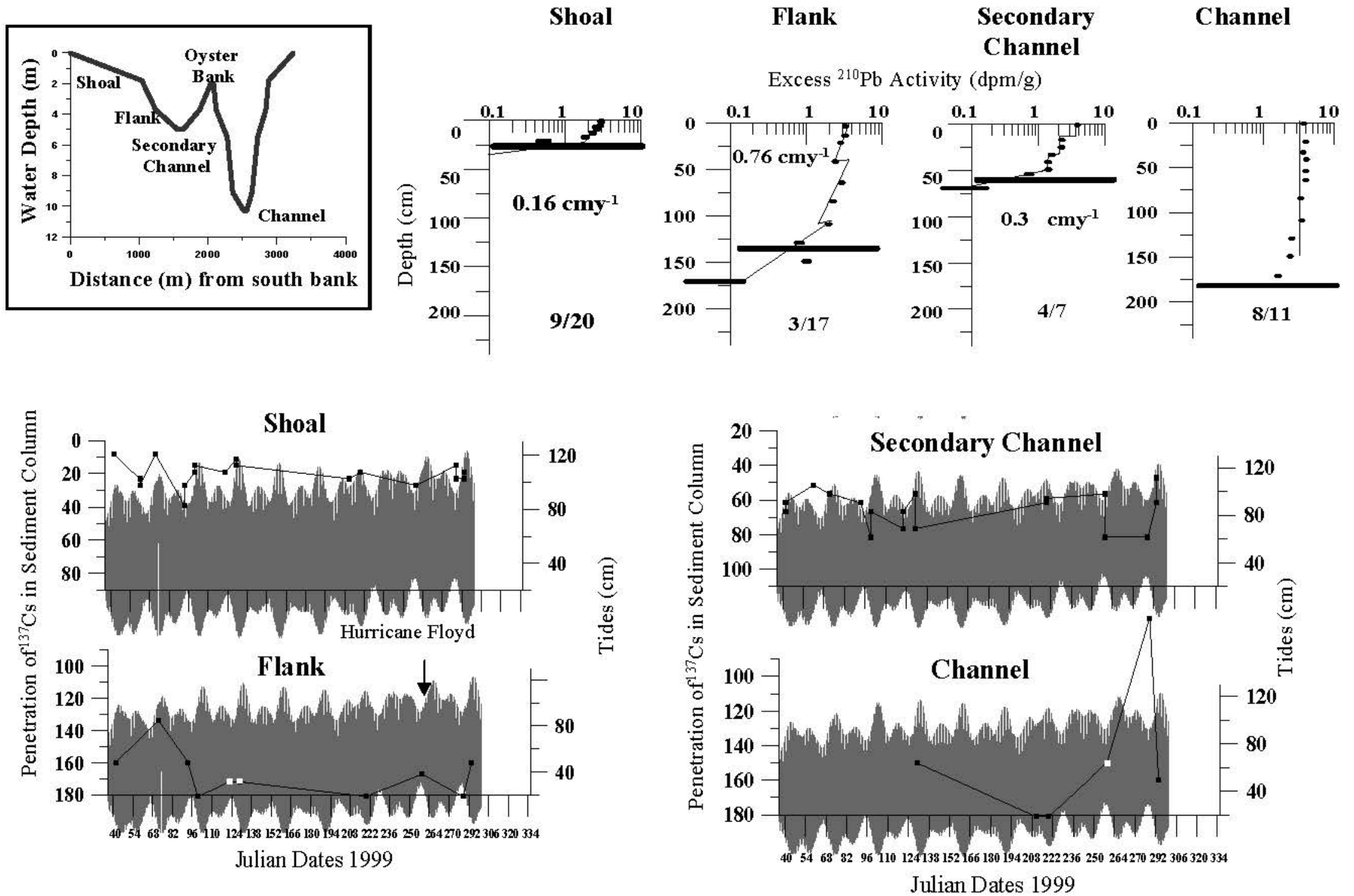


Fig. 1. A cross-section of the upper York River transect with corresponding temporal changes in ^{137}Cs depth of penetration for each subenvironment and representative ^{210}Pb profiles.

Sediment Profiles of PAH

Total pollutant PAH (not including perylene) range from 62-880 ng g⁻¹ at POD and 49-840 ng g⁻¹ at LY (Fig. 2) over the entire depth of the cores (~200-250 cm). Previous studies in the York River (Countway et al., in review) and southern Chesapeake Bay (Arzayus et al., 2001) documented clusters of PAH falling into low molecular weight (<202), alkyl- (MW=192), and high molecular weight (≥180) groupings in both water column particle and sediment samples using principal components analysis (PCA). These groupings reflect PAH sources (petrogenic vs. combustion) and physical-chemical properties that govern their mode of delivery to the water column (gaseous vs. particle deposition). To follow the behavior of these PAHs downcore, the same groupings were retained in this study. Soot PAHs (MW≥202) range from 26-750 ng g⁻¹ at POD and 33-707 ng g⁻¹ at LY (Fig. 2). Volatile PAHs (≤180) constitute less than 10% of the total PAHs in post-1963 sediments and less than 30% in pre-industrial sediments (Fig. 2). Concentrations range from 7-72 ng g⁻¹ at POD and 8-77 ng g⁻¹ at LY. For all three groups of PAH, concentration profiles are not significantly different between the two sites in the upper 45 cm of each core, roughly corresponding to post-1963 depositional period.

In both profiles, subsurface maxima are present (Fig. 2) that most likely correspond to peak PAH emissions in the 1960s. At the base of the cores, concentrations at both sites are similar suggesting they probably represent pre-industrial (c. 1850) concentrations of PAH. However, while sediment PAH profiles are similar in the upper and lower sections of the two sites, a decoupling occurs below 50 cm where PAH at POD attenuate much more rapidly than at LY. It is unlikely that accumulation or penetration of PAHs at POD is substantially less than at LY (Arzayus et al., submitted). However, sediment may have been sufficiently scoured from POD during a large erosional event. In this scenario, a parcel of sediment approximately 100 cm thick would have been removed in order to collapse the two profiles. While this would be an extreme event, it is not unlikely. Dellapenna et al. (1998) observed a decoupling in porosity of 70 cm between two cores collected 9 months apart in the same area as POD. After correcting the porosity profiles with the Cs-137 common datum, it was evident that 70 cm of sediment eroded within less than a year. Similarly, during Hurricane Floyd in 1999, the mixed layer depth in the channel in the upper York decreased by ~1 m between 20 September and 19 October and then increased by ~1 m during the following week (Kniskern, 2001). We suggest that similar extreme erosional event(s) may explain the between-site differences in the PAH profiles.

PAH Isomer Ratios

PAH isomer ratios for surface sediments collected from the York River are comparable to those determined for surface sediments collected from throughout southern Chesapeake Bay (Arzayus et al., 2001) and indicate a common source, coal soot (Dickhut et al., 2000). We also quantified downcore values for PAH isomer ratios to examine whether sources of PAHs changed over time in horizons representing deposition since 1963 (Fig. 3). Downcore profiles of anthracene/phenanthrene, benzo(a)anthracene/chrysene, and benzo(b)fluoranthene/benzo(k)fluoranthene averaged 0.25 +/- 0.02, 1.37 +/- 0.08, and 3.25 +/- 0.26 at POD and 0.31 +/- 0.02, 1.13 +/- 0.16, and 2.93 +/- 0.24 at LY. Because isomer ratios were relatively constant throughout these horizons, we conclude that PAH sources have not likely changed since 1963. We then examined between-site differences in the average values of six PAH isomer ratios calculated for sediments deposited since 1963 (Arzayus et al., submitted). Five of the six isomer pairs were significantly different (p<0.05) at POD vs. LY. We also compared the average downcore PAH isomer ratios for both POD and LY with the average isomer ratio for surface sediments obtained from throughout southern Chesapeake Bay. In all cases but one

((123cd)pyrene/benzo(ghi)perylene), the average PAH isomer ratios of post-1963 sediments at LY are closer to the average of the recently-deposited sediments collected from surface grabs throughout southern Chesapeake Bay. We hypothesize that the observed between-site differences in isomer ratios are due to enhanced microbial activity promoting degradation of solvent extractable PAH or sequestration into bound phases at POD due to the high-energy regime and fluctuating redox conditions. Because sediments are on-average older at POD, we expect that PAHs have been more influenced by biodegradation than at LY resulting in preferential removal of specific PAH isomers.

IMPACT/APPLICATIONS

Our preliminary results show the influence of physical and biological processes on sediment distributions of PAHs in southern Chesapeake Bay. Results from this study provide insights useful in developing models for predicting contaminant behavior in the environment and assessing the risks PAHs deposited in sediments pose to organisms. These results may also be relevant in developing criteria useful in assessing conditions under which natural attenuation may be a useful remediation strategy.

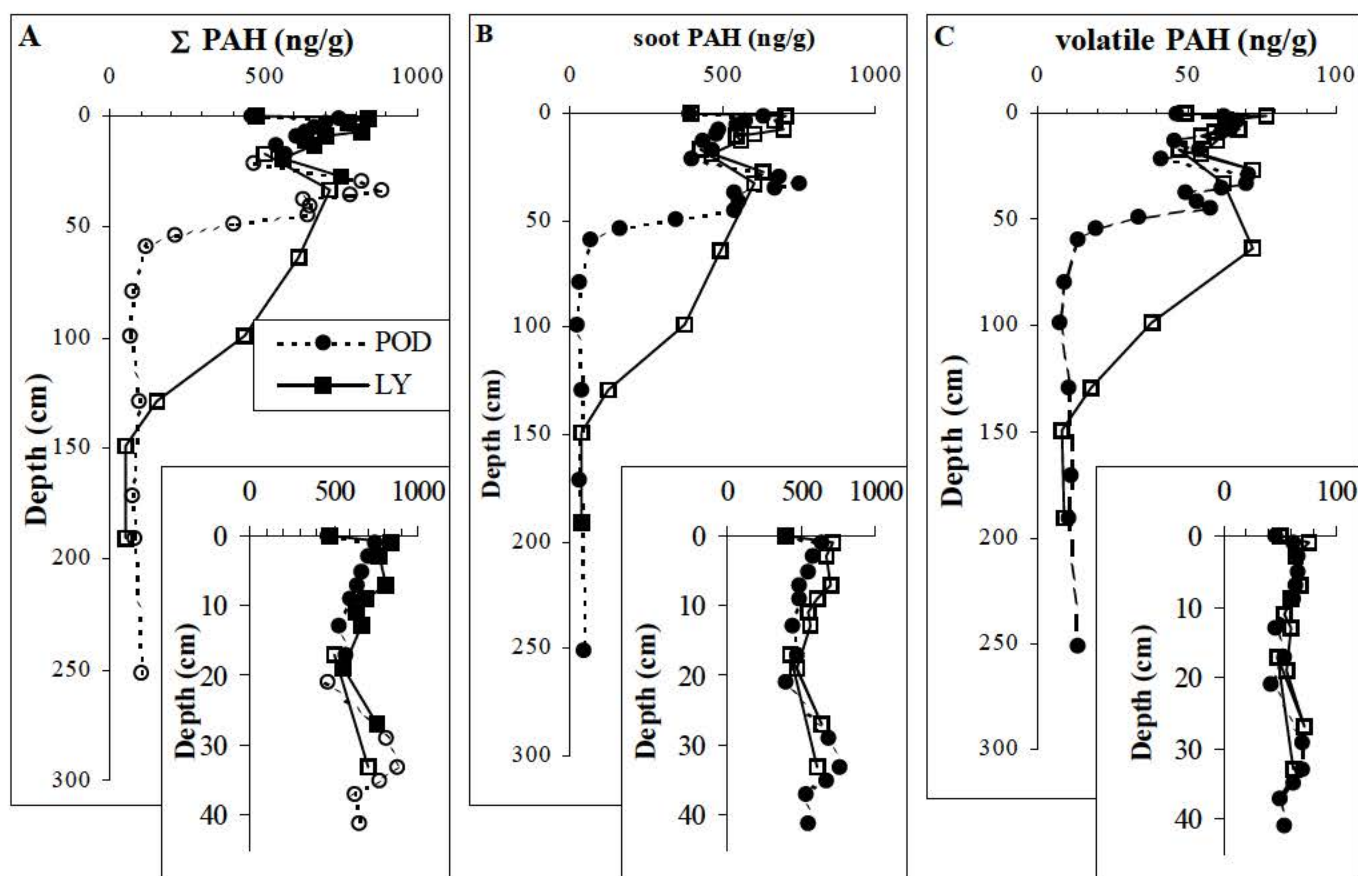


Fig. 2. PAH profiles at POD and LY. Closed symbols are box cores, open symbols are Kasten cores. Inset is a magnification of the upper 45 cm of each core. A) total summed pollutant PAH, B) total summed soot PAH (MW ≥ 202), C) total summed volatile PAH (phenanthrene, anthracene, 1-methylfluorene, and fluorene). Soot and volatile PAH distinguished in Arzayus et al. (2001).

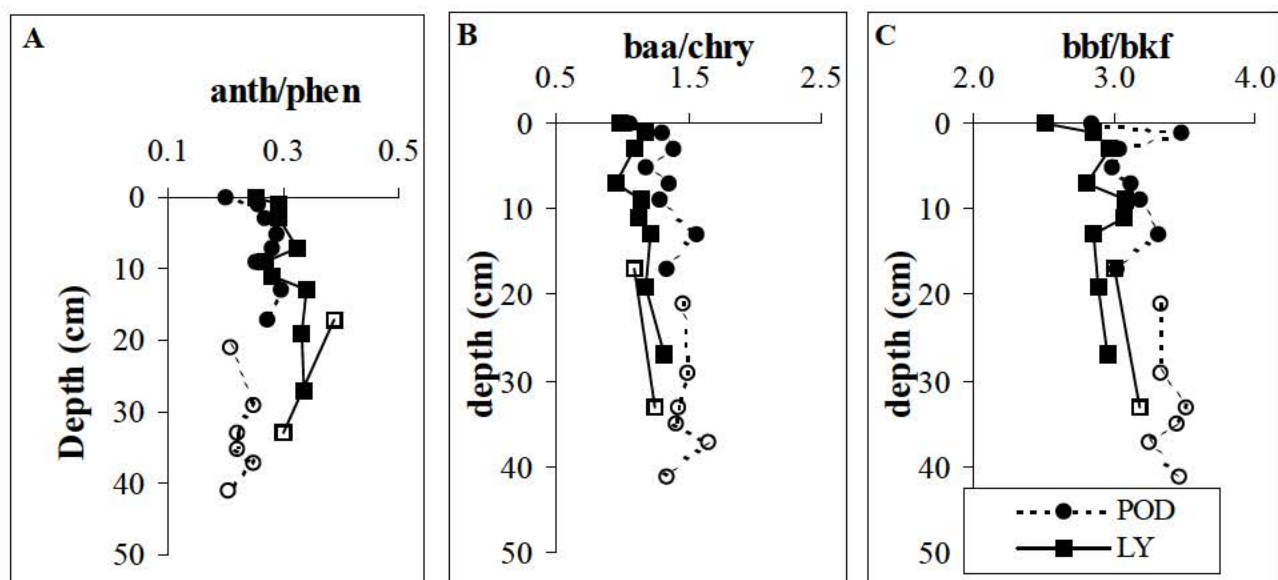


Fig. 3. Select PAH isomer ratios, calculated for the upper 50 cm of each core (POD is the physically energetic site; LY is dominated by bioturbation). Closed symbols are box cores, open symbols are Kasten cores. A) anthracene/phenanthrene, B) benzo(a)anthracene/chrysene, C) benzo(b)fluoranthene/benzo(k)fluoranthene.

TRANSITIONS

Results from this study complement other studies funded through the ONR Harbor Processes in San Diego Harbor, the lower Chesapeake Bay and Elizabeth River, VA. Our investigation into the role of physical energy in influencing sediment distributions of PAHs also complements ONR-supported work in the Hudson River estuary (Geyer and colleagues).

RELATED PROJECTS

A research grant funded through VA Sea Grant and EPA (to R.M.D.) supported related work in the urbanized Elizabeth River, VA estuary.

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